

CELL ANALYSIS, MODELING, AND PROTOTYPING (CAMP) FACILITY RESEARCH ACTIVITIES

Project ID: BAT030

STEVE TRASK

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OVERVIEW

Timeline

Start: October 1, 2014

Finish: September 30, 2021

Percent complete: 80 %

Budget

- \$950K
 - 100% DOE-EERE-VTO

Barriers

- Need a high energy density battery for Electric Vehicle (EV)
 use that is safe, cost-effective, has long cycle life, and meets
 or exceeds DOE / U.S. Drive goals
 - Independent validation analysis of newly developed battery materials are needed in cell formats with at least 0.2 Ah before larger scale industrial commitment

Partners

- Coordinated effort with DOE-EERE-VTO BTMS, Next Generation Anodes, Next Generation Cathodes, ReCell, XCEL (INL, LBNL, NREL, ORNL, PNNL, SLAC, SNL)
- Argonne Facilities: MERF, EADL, CNM & PTF
- See Collaboration list at end



RELEVANCE / OBJECTIVES

■ Transition new high energy battery chemistries invented in research laboratories to industrial production through independent validation and analysis in prototype cell formats
 ➤ xx3450 & xx6395 pouch cells & 18650 cells; ranging from 20 to 3,000 mAh capacity



Researchers are often not able to provide the quantities of novel materials needed to make a full size EV cell to demonstrate the merits of their discoveries. The CAMP Facility is specifically designed to explore new materials with quantities as small as 50 grams for active materials, and even less for electrode/electrolyte additives

FY20 PROGRESS MEASURES & MILESTONES

Milestone	Planned End Date	Туре	Status
Develop methods to fabricate pre-lithiated high-energy electrode couples on pilot-scale coater in dry room (see BAT028)	9/30/2019	Quarterly Progress	Completed
Measure electrochemical performance of LLZO ceramic in symmetric lithium cells as a function of temperature (see BAT028)	3/30/2020	Annual Progress	In progress
Deliver needed experimental electrodes from the CAMP Facility's Electrode Library to research organizations involved in DOE-EERE projects	9/29/2020	Quarterly Progress	On-schedule
Develop methods to direct coat hybrid polymer ceramic coatings/electrolyte membranes onto electrodes and test electrochemically	9/29/2020	Quarterly Progress	On-schedule
Support development of advanced cell systems for Behind The Meter Storage	9/29/2020	Annual Progress	On-schedule

COVID-19 has reduced lab time and may cause delays in completing FY20 milestones



APPROACH / RESOURCES

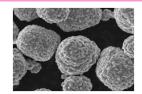
- Researchers submit materials with promising energy density
- Small hand-coated electrodes are made
- Coin cells are made and tested
- Larger material samples are obtained (MERF, partnerships, etc.)
- Longer lengths of electrode are made from scaled materials
- Pouch cells or 18650s are made and tested
- Extensive diagnostics & electrochemical modeling on promising technologies

Glove box Benchtop

Dry Room Pilot scale















TECHNICAL ACCOMPLISHMENTS (NOT ALL PRESENTED AT AMR)

- Completed method development for pre-lithiation of electrodes & graphite powder via electrochemistry (see BAT028)
- Demonstrated successful ultra-thin Li-metal electrodeposition onto copper foil technique in dry room
- Performed molten lithium soldering onto LLZO disk with mixed results (see BAT028)
- Initiated solid-state-electrolyte and hybrid composite polymer scale-up design for roll to roll coating
- Identified mechanisms of cell performance improvement resulting from oxide nanoparticle addition to electrolyte
- Continued process development and post-test analysis of ceramic coatings (as sole electronic insulator) on anode electrodes in preparation for solid-state-electrolyte coatings
- Purchased new multi-functional coating system that enables a variety of advanced coating techniques to perform uniform thin coatings
- Supported numerous DOE projects with prototype electrodes & cells (see BAT251, BAT252, BAT253, BAT386, BAT422, BAT436, BAT456, BAT457, BAT458, BAT459, BAT460, BAT461, BAT462, BAT463, BAT467, BAT469, BAT471)

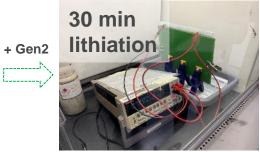
PRE-LITHIATION OF ELECTRODES IN DRY ROOM

SUCCESSFUL LITHIATION OF GRAPHITE AND SILICON-BASED ELECTRODES IN OPEN CONTAINER,

→ CONTINUOUS PROCESS WOULD REQUIRE LARGE FOOTPRINT







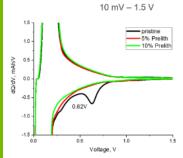


Pristine

5% lithiation

Implies that for an industrial coating rate of 40 m/min, a continuous 60 meter electrode stretch would need to be immersed in electrolyte to achieve 5% SOC at 2C rate

Coin cell verification of pre-lithiated graphite electrode



SEI formation peaks absent in 5% and 10% pre-lithiation and improved 1st cycle coulombic efficiencies suggest the electrode SEI survived DMC washing and handling in the dry room



Pre-lithiated electrodes integrity were not compromised, resulting in no pouch cell assembly process changes

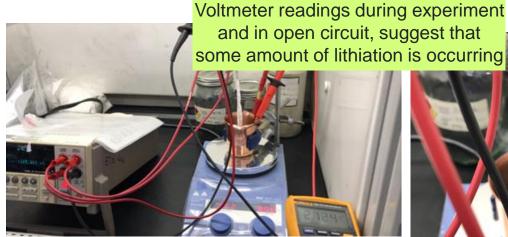


PRE-LITHIATION OF GRAPHITE POWDER IN DRY ROOM

POOR RESULTS FOR LITHIATION OF GRAPHITE POWDER IN BEAKER

Superior Graphite 1506T powder with [Gen2] 1.2 M LiPF₆ EC:EMC (3:7 wt.%)

Li metal ribbon on nickel rod wrapped in separator, copper beaker with stir bar, 2 grams of graphite powder





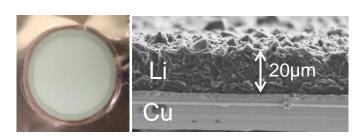
10% lithiation

Pre-lithiated graphite <u>powder</u> -> rinsed with DMC, dried, then made into an electrode for coin cell evaluation

dQ/dV SEI formation peaks present in both the pristine and the 10% pre-lithiation powder, suggesting this method of pre-lithiation needs to be further optimized

LITHIUM METAL ELECTRODEPOSITION PROCESS

THE CAMP FACILITY DRY ROOM WAS USED IN THE DEVELOPMENT OF A NEW ULTRA-FAST LITHIUM METAL ELECTRODEPOSITION PROCESS THAT CAN PRODUCE A SUB-20-MICROMETER THIN LITHIUM METAL ANODE

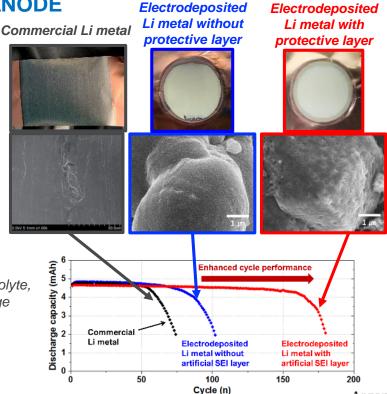


A photo (left) and SEM image (right) of electrodeposited Li-metal

Artificial protective SEI layer is simultaneously generated on the top of Limetal during this process

3 to 4.25 V, cycling test: vs. LCO cathode, Gen2 electrolyte, 0.2C charge/0.5C discharge

Data will be fit to semi-empirical model to provide correlation for use in BatPaC



SOLID-STATE-ELECTROLYTE CANDIDATES

Solid-state-electrolyte (SSE) effort within the CAMP Facility is focused on conductivity, stable voltage window, and fabrication scalability.

Conductivity of solid state electrolytes at room temperature:
 Li₃CIO > sulfide > Li₃N > LLZO(Garnet) ~ 10⁻³

	LLZO	Sulfide	Ba-Li ₃ CIO
Conductivity (RT, mS/cm)	1~1.5	1~40	> 10
Voltage Window (V vs. Li/Li+)	0.05~2.9 (3.3)	1.7~2.1 (2.5)	0~8
Pros	Stable in ambient environment	High conductivity	Easy scale-up
Cons	Li dendrites grow inside	Unstable with O ₂ , H2O H ₂ S formation	Corrosive

Coating of ceramic slurry film over anode



CAMP Facility FY19 AMR





COATING SOLID-STATE-ELECTROLYTE MEMBRANES

LLZO Free-standing Membrane

- Mix and ball-mill: LLZO / polyvinyl butyral / benzyl butyl phthalate / acetone / ethanol to make slurry.
- Tape cast the slurry on Mylar substrate
- Dry and peel off the green films
- Sinter the film at 1080°C in N₂

LLZO Casting on Cathode

- Cathode prepare: casting the slurry of NMP, LLZO, LFP, Super P and PVDF onto Al foil, dried at 80°C overnight
- SSE slurry: LiTFSI/LLZO/SPEEK-PSI-Li (adhesives) in NMP and surfactant
- SSE film direct casting: Tape cast the slurry onto a cathode electrode and dry it at 80°C in argon atmosphere for overnight

<u>Li₆PS₅CI Free-standing Membrane</u>

- Mix Li₆PS₅Cl and acrylate-type binder (1 wt%) in xylene and anhydrous isobutyl isobutyrate
- Coat the slurry on polyethylene terephthalate film and dry the film at 50°C

LiZO-coated NMC Cathode

- Mixing lithium methoxide, zirconium and NMC powder in propanol to prepare LiZO coated NMC powder
- The composite cathode was fabricated by mixing LiZO-coated NMC, SSE, carbon nanofibres and PTFE in dehydrated xylene followed with dry film process
 LiZO = Li₂O-ZrO₂



HYBRID COMPOSITE POLYMER SCALE-UP

TRIAL ROLL-TO-ROLL COATING OF SOLID-STATE-ELECTROLYTE

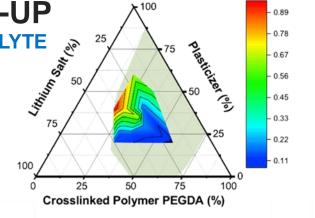
	Monomer	Initiator	Li Salt	(Solid) Plasticizer
1	PEGDA	AIBN	LiTFSI	SN
2	PEGDA	BAPOs	LiTFSI/LiBOB	GN

PEGDA = Poly(ethylene glycol) diacrylate AIBN = 2,2'-azobisisobutyronitrile BAPOs = Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide

SN= Succinonitrile GN= Glutaronitrile

Advantages for Solid Polymer Electrolyte

- High energy input process can be avoided such as high temperature sintering
- The technique of thin polymer membrane fabrication and coating on the electrode laminate aligns well with the current CAMP Facility capabilities
- The polymer based solid electrolyte provides the flexibility in the formulation to be compatible with different electrode materials



Kewei et al. Joule 2018, 2, 1-19

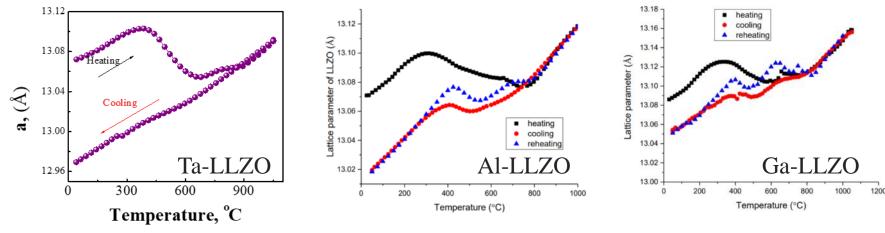
- Initial coating effort will use PEGDA, a thermal initiator, and LiTFSI salt
- Materials have been acquired and trial coating will be made when we resume lab operations
- Coating results will provide valuable information for continued studies to incorporate other variables such as singleionic conducting solid-state-electrolytes, UV initiators, crosslinkers, and plasticizers



Ionic conductivity (mS/cm)

PROCESS CONSIDERATIONS WHEN USING LLZO

ELECTROCHEMICAL COMPATIBILITY OBSERVED FOR LLZO CO-SINTERED WITH NMC622, HOWEVER DIRECT USE OF LLZO REQUIRED THERMAL PROCESSING



- In situ high energy diffraction was carried out during the thermal processing of Ta, Al, and Ga doped LLZO
- All as-received doped LLZO samples exist as a cubic form
- LLZO powders potentially convert to a low temperature cubic form (H intercalation phase) after storage
- All materials experience irreversible phase transformation between 300°C and 700°C
- Ta-LLZO can recover after the initial thermal processing. However, both Al-LLZO and Ga-LLZO only partially recover after the thermal processing
- Thermal processing should be considered for LLZO powders before direct use



ALTERNATIVE SLURRY POLYMER & SOLVENTS EXPLORED

SLURRY PROCESSING ISSUES HAVE BEEN OBSERVED WITH SOME HIGHER NI CONTENT CATHODES, SOLID-STATE-ELECTROLYTES, AND SILICON

Polymers

- PVDF
- CMC
- SBR emulsion
- PAA
- LiPAA
- EVOH
- PVA
- PEG
- Xanthan gum

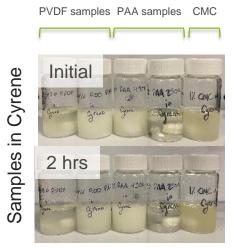
pH Adjustment

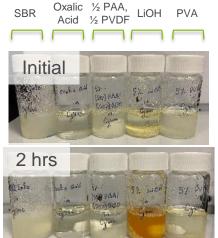
Additives

- LiOH
- NH₄OH solution
- Oxalic acid

Solvents

- NMP
- Water
- Cyrene





5 wt.% LiOH in Cyrene changed notably in color and gelled, indicating the combination in a slurry should be avoided

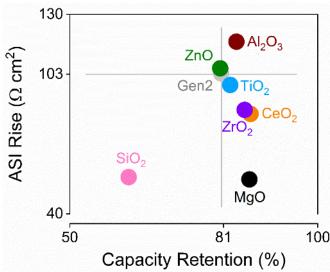




ELECTROLYTE MODIFICATION BY CERAMIC NANOPARTICLES

SCAVENGING WATER FROM THE ELECTROLYTE (AND NOT HF) LIMITS ASI RISE OF NMC811





- Ceramic nanoparticles added to Gen2 electrolyte (30 mg/mL)
- Electrolyte "aged" for 7 days
- Tests in NMC811//graphite cells

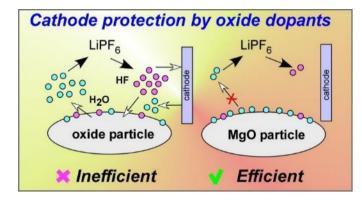
NMR analyses of <u>electrolyte +</u> <u>ceramics</u> exposed to 8,300 ppm water for one week

varying degree of success in controlling electrolyte hydrolysis

Electrolyte/ ceramic	% LiPF ₆ hydrolyzed	% HF yield
baseline	4.0	9.7
SiO ₂	10.4	4.1
ZnO	9.9	9.0
ZrO_2	7.4	13.5
TiO ₂	7.1	11.9
Al_2O_3	6.5	9.4
CeO ₂	4.8	9.0
MgO	0.1	0.0

MgO is a more efficient drying agent than other ceramics, scavenging moisture before it can react with LiPF₆ to form HF

Solely harvesting HF will release H₂O in the electrolyte, which generates more HF. Water scavenging, on the other hand, can mitigate HF generation. This is what makes MgO an effective additive, protecting NMC811 particles from HF attack



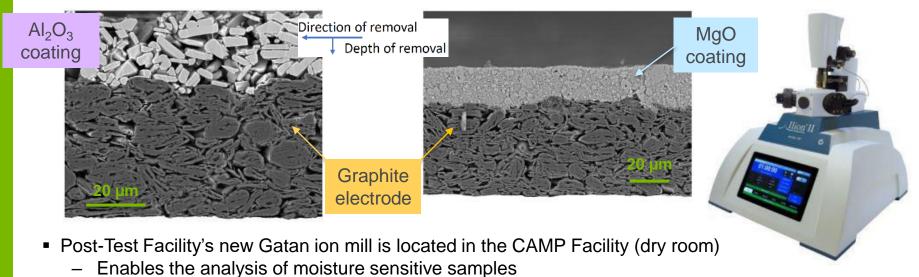
Rodrigues et al., ACS Appl. Energy Mater. 2019, 2, 8, 5380-5385



POST-TEST FACILITY ION MILL OF CERAMIC COATINGS

INITIAL RESULTS INDICATE CLEAR CERAMIC COATING // GRAPHITE ELECTRODE INTERFACE

Intriguing scoping results of half and full cells made with a range of ceramic coatings (see FY19 BAT030)
 prompted post-test analysis of the ceramic coating (sole electronic insulator) // graphite electrode interface



- Ceramic-based slurry appears to be laying on the graphite electrode, and not filling anode porosity
- Technique able to provide views of graphite plane edges (useful for examining the SEI)
- Sets the stage for efforts to acquire ceramic materials with more favorable particle sizes and morphologies that result in uniform thin (>20 μm) ceramic coatings to continue post-test investigations

NEW MULTI-FUNCTIONAL COATING SYSTEM PURCHASED

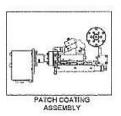
SIGNIFICANTLY ENHANCES THE RANGE OF COATING METHODS AT THE CAMP FACILITY, ENABLING UNIFORM THIN CERAMIC COATINGS AND ELECTROLYTE MEMBRANES

Interchangeable coating heads

 Gravure and dual slot die methods provide greater flexibility for layered coatings



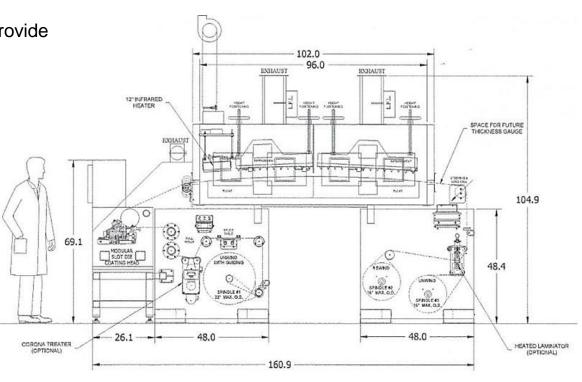






Additional Capabilities Available:

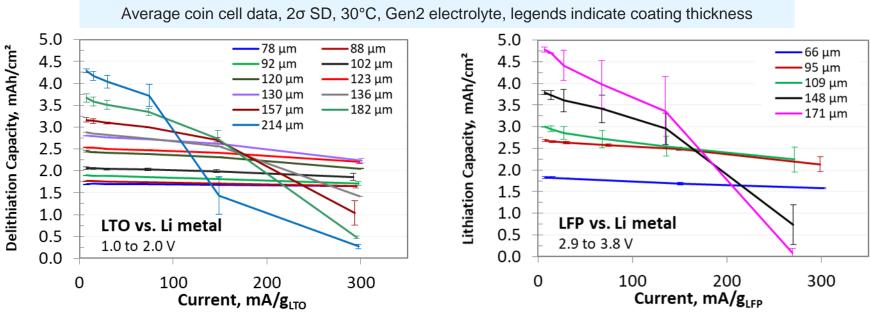
- Progressive cavity pump
- Corona treatment
- Thermal laminate module
- Dry Thickness gauge





SUPPORT OF BEHIND THE METER STORAGE PROGRAM

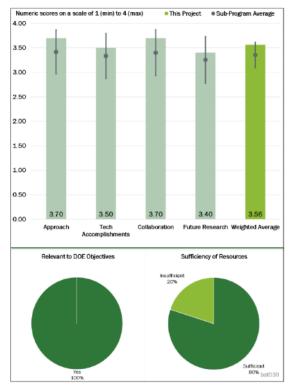
INVESTIGATED IMPACT OF ELECTRODE THICKNESS ON PERFORMANCE AND PROVIDED COST MODELING CALCULATIONS FROM BATPAC



- Demonstrated high areal capacities at slower rates, however faster rates for thicker coatings resulted in loss of electrode utilization
- BatPaC calculations, incorporating slow rate data generated from increasing coating thicknesses, suggest increased energy densities and cost savings for thicker electrodes

REVIEWER COMMENTS FROM 2019 ANNUAL MERIT REVIEW

- "The reviewer commented that the program is very important for new materials innovation and evaluation and fills the gap between industry and academia."
- This was a common response among the 5 reviewers.
- "The reviewer recommended looking at expanding the library into higher areal capacity electrodes."
- While the present electrode library is intentionally designed to be ~2 mAh/cm² to minimize thickness effects for novel materials that require validation and provide baseline standardization, the CAMP Facility regularly coats electrodes at higher areal capacities when warranted for larger cell demonstration and provides these electrodes as needed for programmatic research (examples include BAT422 [BTMS], BAT436 [Silicon], BAT386 [XCEL], BAT467 [ReCell]).
- "The coating work is also interesting to the reviewer, but given the challenges in producing a uniform quality coating, it is too early to determine its benefits."
- We find the ceramic coating work intriguing, as well, and look forward to applying and examining these uniform coatings using the recently purchased coater that will enhance our coating technique capabilities (see slide 17). The initial efforts have been informative and the new multi-functional coater will be critical in the development of solid-state-electrolyte cells at the CAMP Facility.
- Several of the reviewers commented that "list of collaborators is impressive; however, the inclusion of some major battery manufacturers, if possible, would be desirable."
- We agree and welcome collaborations with battery manufacturers.



2019 Annual Merit Review, Vehicle Technologies Office Results Report, February 2020



CAMP FACILITY'S ELECTRODE LIBRARY

SUPPORTING THE EERE-VTO R&D BATTERY COMMUNITY

- The Electrode Library serves as a supply of standard electrode samples that are designed to be interchangeable with one another (capacity matched)
- Electrodes can be made with as little as 50 g of experimental material, and can be made to match an existing counter electrode

Currently Available:

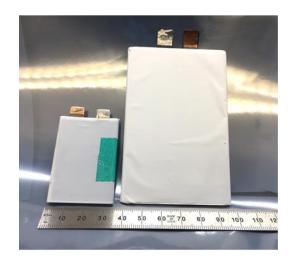
- 15 anodes
- Neg:Pos balanced
- 19 cathodes
- Anodes at 2 mAh/cm²
- 220 mm x 110 mm of coating per sheet

	FY17		FY18		FY19		FY20 (as of April 2020)	
Argonne	142	9 %	140	14.3 %	160	15.0 %	125	24.1 %
Other National Labs	172	11 %	172	17.5 %	224	21.0 %	174	33.6 %
Universities	151	10 %	175	17.8 %	296	27.7 %	137	26.5 %
Industry	1083	70 %	495	50.4 %	388	36.3 %	82	15.8 %
Total:	1548		982		1068		518	

CAMP FACILITY'S POUCH CELL DELIVERIES

SUPPORT OF VTO PROGRAMS CONTINUES TO INCREASE

- Pouch cells provide critical information on the scalability of newly developed battery materials
- CAMP pouch cell format capabilities of xx3450 and xx6395, as well as customized designs to enable specialized scoping methods
- xx3450 cells range from single-layer (~20 mAh)
 to multi-layer (~600 mAh)
- xx6395 cells range from single-layer (~70 mAh)
 to multi-layer (~3000 mAh)







	FY17	FY18	FY19	FY20 (as of April 2020)
Pouch Cells Delivered	55	162	300	175



CAMP FACILITY COLLABORATIONS

Majority of these collaborations over the past several years are centered on the CAMP Facility providing electrodes and cells







REMAINING CHALLENGES AND BARRIERS

- Resolve non-ideal rheological slurry/coating behavior when they are encountered (gelation, phase separation, agglomerates, aggregates, etc.)
 - Use learned processing knowledge from high pH (>12) cathode powders and from specialty coatings to other materials such as active materials or polymer films
- Apply direct coating roll-to-roll options needed to effectively coat ceramic materials onto (solid-separator) and in electrodes (solid-state-electrolyte)
 - Application of films via single slot die, dual slot die, gravure, knife-over-roll, etc.
 are needed to be demonstrated with the new multi-functional coating system
- Increased electrode thicknesses may impact electrode utilization at higher rates
 - Electrode design optimization at the CAMP Facility is restrained in scope of work but warranted to select programs and materials where potential performance improvements are promising

PROPOSED FUTURE RESEARCH

- Leverage the new multi-functional coating system to apply uniform thin (<20 μm)
 ceramic composite coatings on anodes, on separators, and as free-standing films
- Complete alternative polymer/solvent study to enhance the slurry processing compatibility of ceramics (esp. LLZO)
- Determine if LLZO materials need pre-treatment before coating
- Demonstrate hybrid ceramic-polymer composite scale-up and performance
- Continue coordinating with the Post-Test Facility to examine the ceramic//graphite electrode interface to determine possible failure mechanisms and validity, with the assistance of BatPaC, of relying solely on a ceramic coating as the sole electronic insulator (without polymer separator present)
- Continue to support DOE-EERE-VTO programs
- Any proposed future work is subject to change based on funding levels



SUMMARY

- Completed study of fabricating pre-lithiated electrodes and graphite powder in the dry room
- Characterized LLZO materials to determine thermal treatment effects on phase purity
- Showed that oxide nanoparticles, which scavenge water from the electrolyte, can lower cell capacity fade and impedance rise
- Purchased a multi-functional coating system
 - System will provide coating method flexibility (i.e. single slot die, dual slot die, gravure, knife-over-roll), enhancing our ability to create uniform solidstate-electrolyte and ceramic separator films/coatings onto electrodes
- Provided support to the Behind The Meter Storage program for development of advanced cell systems
- Supplied numerous experimental electrodes and cells to DOE programs



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- Post-Test Facility (PTF)
- Electrochemical Analysis and Diagnostic Laboratory (EADL)
- Center for Nanoscale Materials (CNM)
- Advanced Photon Source (APS)

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TECHNICAL BACK-UP SLIDES

The following slides are available for the presentation and included in the Web PDF files released to the public.

No Technical Back-up Slides

